PB86-193687

Laboratory Study to Evaluate the Impact of NOx, SOx, and Oxidants on the Atmospheric Corrosions of Galvanized Steel

Northrop Services, Inc.
Research Triangle Park, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-193687

EPA/600/D-86/095
May 1986

A LABORATORY STUDY TO EVALUATE THE IMPACT OF NO_x, SO_x, AND OXIDANTS ON THE ATMOSPHERIC CORROSIONS OF GALVANIZED STEEL

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Contract No. 68-02-4033

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SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-86/095		

4. TITLE AND SUBTITLE	5. REPORT DATE
A LABORATORY STUDY TO EVALUATE THE IMPACT OF NO_x, SO_x AND OXIDANTSON THE ATMOSPHERIC CORROSION OF GALVANIZED STEEL	May 1986
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
E.O. Edney, D.C. Stiles, J.W. Spence, F.H. Haynie and W.E. Wilson	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Northrop Services, Inc. P.O. Box 12313 Research Triangle Park, NC 27709	CCVN1A/09-3179 (FY-86)
	11. CONTRACT/GRANT NO.
	68-02-4033
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Atmospheric Sciences Research Laboratory— RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO THE PUBLIC	UNCLASSIFIED	33
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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ABSTRACT

A series of laboratory experiments was conducted in which galvanized steel samples were exposed to NO_2 in air and irradiated propylene/nitrogen oxides/air mixtures in the absence and presence of SO_2. Dew was produced periodically on the test panels, and at the end and/or during the experiments, panels were sprayed with either deionized water or an ammonium bisulfate solution (pH of 3.5). Gas phase concentrations were monitored, and dew and rain rinse samples were analyzed for nitrite, nitrate, sulfite, sulfate, formaldehyde, and zinc.

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INTRODUCTION

Galvanizing steel is a well-known technique for protecting steel against corrosion. Galvanized steel consists of a zinc (Zn) coating strongly bonded to a steel substrate. Zn is anodic with respect to iron and will react electrochemically before iron in the presence of an electrolytic solution. Because it is one of the least expensive methods for protecting steel against atmospheric corrosion, a number of field studies have been conducted to measure the atmospheric corrosion rate of galvanized steel and/or Zn (1-11). Many of the studies have focused on the effect of SO_2 and time of wetness on the corrosion rate. While these parameters clearly play an important role in corrosion, any model based solely on these parameters is likely to be incomplete because the effects of wet deposition and dry deposition of other air pollutants have been neglected.

Recent studies have shown that the deposition of a compound rather than the concentration should be used to assess the impact of SO_2 or other compounds on atmospheric corrosion (9,11-12). The dry deposition D_x of a reactive species x is defined by the following relationship:

$$D_x = \int_0^{t_e} F_x(t)dt, \tag{1}$$

where

t_e = exposure time, and
$F_x(t)$ = the molar flux at time t, i.e.,

$$F_x(t) = [x(t)]v_d, \tag{2}$$

where

$[x(t)]$ = the gas phase concentration at time t, and
v_d = the dry deposition velocity.

One approach to developing a corrosion model for galvanized steel based on dry deposition is to assume that the corrosion C (in moles of Zn lost per unit area) can be represented as a linear combination of the corrosion induced in a clean air environment and that associated with air pollutant x, i.e.,

$$C = (A + \gamma[x]v_d)t_w, \tag{3}$$

where

t_w = the time of wetness,
A = a constant, and
γ = number of moles of Zn corroded per mole of x deposited.

If no antagonisms or synergisms occur, Equation (3) can be extended to include the effects of other compounds by converting the second term to a sum over all pollutants depositing onto the surface. Equation (3) assumes that deposition takes place only when the surface is covered by a film of moisture.

The inability to estimate dry deposition velocities and the lack of knowledge of the compounds that are likely to contribute to corrosion makes Equation (3) difficult to apply in evaluating corrosion data. The results of the experiments reported here will address both of these issues and will be used to develop the framework for a model for analysis of galvanized steel corrosion data obtained from field studies.

In the presence of a moisture film, but in the absence of pollutants other than CO_2, the effective operative electrochemical reactions taking place on a wet galvanized steel surface are believed to be (13)

$$\text{Anode} \quad Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e^-$$

$$\text{Cathode} \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$

The zinc hydroxide ($Zn(OH)_2$) formed will react with dissolved CO_2 to produce zinc carbonate ($ZnCO_3$), a compound that is slightly soluble in water, i.e., solubility = 80 nmol/ml in water at 15°C (14). Buildup of the insoluble corrosion products such as $Zn(OH)_2$ and $ZnCO_3$ will create a protective layer that serves to inhibit further corrosion. The corrosion rate will then be small unless there is some means for either preventing the formation of the protective layer or destroying it once it has formed.

The details of the mechanism for SO_2-induced corrosion of galvanized steel have not been established; however, it is likely that the corrosion process is initiated by the reaction of Zn with the sulfurous (H_2SO_3) and sulfuric (H_2SO_4) acids generated in the dew. In particular, H_2SO_4 will react with either the base metal or the protective corrosion products, $ZnCO_3$ or $Zn(OH)_2$, producing soluble zinc sulfate ($ZnSO_4$) that has limited protective properties. Dissolution of the protective layer will stimulate further electrochemical corrosion which will tend to reform the insoluble layer. The extent of formation of the protective layer is determined by the SO_2 deposition to the surface. In clean air environments, a thick adhesive protective layer will form, whereas in polluted areas of high SO_2 concentrations only a very thin layer will be produced (15).

The production of soluble $ZnSO_4$ suggests that the precursor to the anion, gas phase SO_2, accelerates corrosion. *Based on this mechanism, it is likely that other air pollutants that readily adsorb on a surface, producing acidic compounds that can react with the corrosion products to form soluble Zn compounds, can accelerate the corrosion rate.*

The objective of this study was to determine whether air pollutants other than SO_2 accelerate the atmospheric corrosion rate of galvanized steel. Short-term laboratory experiments were conducted in which galvanized steel panels were exposed to the following mixtures in air: (1) NO_2, (2) irradiated propylene/nitrogen oxides (C_3H_6/NO_X), and (3) irradiated $C_3H_6/NO_X/SO_2$. The test panels were chilled below the dew point periodically to produce dew. Dew samples were collected and analyzed for Zn and their anion composition. To investigate the impact of acidic wet deposition, during some of the experiments, panels were removed periodically from the chamber and sprayed with either deionized water or dilute solutions of ammonium bisulfate (NH_4HSO_4) (pH of 3.5). The results of these experiments, as well as the framework for a corrosion model for galvanized steel, are presented in this paper.

EXPERIMENTAL

The exposure system consists of two exposure chambers in parallel, coupled to an 11.3-m^3 aluminum and Teflon smog chamber (Figure 1). Light banks are located on two sides of the smog chamber and consist of 56 black lamps and 9 sun lamps. The smog chamber, operated as a continuous stirred tank reactor (CSTR), serves as a reservoir for the exposure chambers. Ambient air first passes through a clean air train, where pollutants and H_2O are removed, and then through a glass manifold where it is mixed with reactants to the desired concentration before entering the smog chamber. The flow rate through the smog chamber is 95 Lpm, producing a residence time of 112 min. Steam is injected into the chamber by the dew point control system that is programmed to maintain the air dew point at 15°C. The air temperature is not controlled.

A cross-sectional drawing of one of the exposure chambers is shown in Figure 2. The chambers are constructed of clean Teflon glued to a 13 x 13 x 152-cm welded aluminum frame. Glass piping is used to connect the exposure chambers to the smog chamber. Both exposure chambers have seven positions for mounting test panels. Each exposure position has a chiller back plate with supplied coolant so that the panel can be chilled below the air dew point to produce dew on the panels. Individual positions can be disconnected from the coolant manifold to remain dry. The coolant temperature enables dew to form in a sufficient quantity to drop into the collection trough below each panel. The collected dew then drains into a Nalgene bottle. The exposure chambers are also equipped with heating lamps. Blowers were mounted on the exposure chambers to maintain turbulent conditions (Reynolds number ~30,000 in the chambers), and the blower settings were selected to produce wind speeds of approximately 300 cm/s (~7 mi/h) in each chamber.

The galvanized steel panels were 8 x 13-cm Zn-coated (hot-dipped), 20-gauge steel plates. The average thickness of the coating was 20 μm, and the exposed surface area per panel was 84.7 cm^2. Before each exposure experiment, the panels were first cleaned by immersion into a 10% by weight solution of ammonium chloride (NH_4Cl) at a temperature of 60°-80°C for 2 min. The panels were rinsed in deionized water and then dried in methanol to remove the moisture.

During and/or at the completion of some of the exposure experiments, galvanized steel panels were sprayed with either deionized water or an NH_4HSO_4 (pH 3.5) solution. The deionized water quickly equilibrated with CO_2 in the laboratory air, producing a value of 5.6 for the pH. By removing the panels from the exposure chambers and mounting them into a Teflon rack, each panel could be sprayed with a specific volume of either deionized H_2O or an NH_4HSO_4 solution. The spray runoff was collected for chemical analysis. For a typical spray condition, ~10 s was the average residence time of a droplet on the surface, whereas the corresponding time for a dew droplet was ~1 h.

The galvanized steel panels were exposed to air masses that contained NO_2 and irradiated mixtures of C_3H_6/NO_X and $C_3H_6/NO_X/SO_2$. A brief description of the protocol used for each of the three experiments is presented.

The NO_2 exposure was a short-term experiment where the panels were exposed to a mixture of 649 ppb NO_2 in air. The total exposure time was 25 h. The microprocessor-controlled chiller system was used to generate two 7-h periods where the panels were covered with dew. The two wet periods were separated by a 5-h dry period. NO_X concentrations were monitored continuously. At the end of the experiment, the panels were sprayed with either 50 mL of deionized H_2O or NH_4HSO_4 solution (pH = 3.5). The volume of collected dew was determined. The dew was then analyzed for NO_2^-, NO_3^-, $SO_3^=$, and $SO_4^=$ by ion chromatography and for Zn by atomic absorption spectroscopy. The rain rinse was analyzed in a similar way.

The C_3H_6/NO_X + hv experiment was a 14-day exposure which consisted of two 7-h dew periods per day separated by 5-h dry periods. Panels were weighed both prior to the experiment and at the completion of the experiment after the corrosion products were removed using the cleaning procedure described above. A correction to the Zn weight loss was made to account for the loss of base metal during cleaning. Panels were exposed to (1) dew only, (2) dew plus acid rain, and (3) dew plus clean rain conditions. The panels exposed under conditions 2 and 3 were removed from the exposure chambers after four and nine days of exposure and sprayed with either 400 mL of deionized H_2O or NH_4HSO_4 (pH of 3.5) solutions. The panels were also sprayed at the end of the experiment. Dew samples were collected daily and analyzed. The NO_X and O_3 concentrations were monitored continuously and peroxyacetyl nitrate (PAN), nitric acid (HNO_3), and aldehyde concentrations were measured during both dry and wet periods.

The exposure conditions for the $C_3H_6/NO_X/SO_2$ + hv experiment were essentially the same as those used in the NO_2 experiment. The exposure period contained two 7-h wet periods separated by a 5-h dry period. All species measured in the C_3H_6/NO_X experiment were measured and, in addition, gas phase SO_2 concentrations were determined as well as $SO_3^=$ and $SO_4^=$ in the dew. No rain data were obtained for this experiment. To investigate the deposition of reaction products of an irradiated $HC/NO_X/SO_2$ mixture during dry periods, one panel was kept dry during the entire exposure.

NO_X concentrations were measured using a Bendix $NO/NO_2/NO_X$ analyzer. The analyzer was calibrated with a certified standard of NO in N_2 obtained from MG Scientific. Ozone was measured on a Bendix ozone analyzer calibrated using a Dasibi Environmental Corporation ultraviolet (UV) ozone generator. Formaldehyde (HCHO) and acetaldehyde (CH_3CHO) were measured by using the DNPH/high performance liquid chromatography technique (16). Calibrations were performed by

using diluted solutions of twice-recrystalized hydrazone samples for each aldehyde. PAN was determined with an Analog Technology Corporation electron capture detector after separation on a packed column containing 10% Carbowax 400 on 80/100 Supelcoport operated at room temperature. The instrument was calibrated according to the procedure described by Lonneman *et al.* (17). SO_2 concentrations were determined using a Thermo Electron Corporation SO_2 monitor. The instrument was zeroed using clean air that had passed through brominated charcoal, reducing the SO_2 concentration to less than 0.5 ppb. An SO_2 permeation tube was used to calibrate the instrument. A CTE dew point hydrometer was used in the dew point control system and was calibrated with a saturated solution of sodium bromide (NaBr) (relative humidity = 58% at 20°C). Chamber HNO_3 concentrations were measured by drawing ~500 L of air through a 25-mm nylon filter (1-μm pore size), extraction of the filter with 10^{-5} M perchloric acid solution, and analysis of nitrate (NO_3^-) by ion chromatography.

The collected dew and rain rinse samples were analyzed for HCHO using the chromotropic acid method. In addition, the samples were analyzed for nitrite (NO_2^-), NO_3^-, sulfite ($SO_3^=$), and $SO_4^=$ using ion chromatography. The analysis was performed on a Dionex Auto Ion System 12 ion chromatograph with a 6-mm x 250-mm fast run anion separator column. Calibrations curves for $SO_3^=$ and $SO_4^=$ were obtained using anhydrous sodium sulfate (Na_2SO_4) and sodium sulfite (Na_2SO_3) salts diluted with deionized H_2O. The $SO_3^=$ standards required an addition of 0.7% HCHO to the stock solution to deter oxidation of $SO_3^=$ to $SO_4^=$. NO_2^- and NO_3^- calibration curves were obtained by diluting the corresponding Na salts in deionized H_2O. The collected dew and rain rinse samples were analyzed for Zn using an Instrument Labs, Inc. atomic absorbance analyzer. The instrument was calibrated by measuring the absorbance of a series of American Chemical Society certified Zn standards.

DATA REDUCTION

Analysis of Gas Phase and Dew Data

In principle, the amount of compound that deposits onto the panels during a wet period can be calculated two ways: (1) by using the difference in the gas phase concentrations during the dry and wet periods, or (2) by employing the concentration of the compound in the dew and the volume of dew. Deposition to a dry panel can also occur, but, as will be shown, for the majority of the compounds reported here, most of the deposition took place in the presence of dew. Therefore, emphasis will be placed on calculating the deposition during wet periods.

During wet periods, the gas phase concentrations decreased due to uptake by the panels. The time dependence of the gas phase concentration of species x during a period of dew formation can be approximated by the following equation:

$$\frac{d}{dt}[x(t)] = \frac{[x_d]}{\tau} - \left(k + \frac{1}{\tau}\right)[x(t)], \tag{4}$$

where

t = time parameter ($t = 0$ corresponds to the onset of dew formation for the wet period under investigation),
$[x(t)]$ = gas phase concentration, and
$[x_d]$ = steady concentration of x during the preceding dry period.

The residence time τ is equal to V_s/Q, where Q is the flow rate through the smog chamber and V_s is the total volume of the system (smog chamber plus exposure chambers). The effective first-order rate constant for deposition to the panel is k and is equal to $\frac{v_d^{(1)}A}{V_s}$ where $v_d^{(1)}$ is the dry deposition velocity and A is the total area of the wet panels. The solution to Equation (4) is as follows:

$$\frac{[x(t)]}{[x_d]} = \frac{1}{1 + k\tau} + \frac{k\tau}{1 + k\tau} \exp[-(1 + k\tau)t/\tau]. \tag{5}$$

Equation (5) can be further reduced if t is chosen such that the second term can be neglected. Under

these circumstances, the panels remain wet long enough for a new steady state condition to be obtained; i.e., for $t/\tau \geq 2$,

$$[x(t)] \approx \frac{1}{1 + k\tau}[x_d] = [x_w]. \tag{6}$$

Steady state concentrations were reached during the exposure experiments reported here since the time of wetness per cycle was 420 min and the residence time was 112 min. An expression for the dry deposition velocity $v_d^{(1)}$ is immediately obtained from Equation (6), i.e.,

$$v_d^{(1)} = \frac{Q}{A}\left(\frac{[x_d]}{[x_w]} - 1\right). \tag{7}$$

Use of Equation (7) is limited by the accuracy of the measurement of the decrease in the gas phase concentration and in practice can only be used to calculate dry deposition velocities of compounds that readily absorb onto the surface.

The amount of material deposited during a wet period is found by integrating the expression for the molecular flux over time, i.e.,

$$D_x^{(1)} = \int_0^{t_w} v_d^{(1)}[x(t)]dt = \frac{v_d^{(1)}[x_d]\tau}{1 + k\tau}\left\{\frac{t_w}{\tau} + \frac{k\tau}{1 + k\tau}(1 - exp[-(1 + k\tau)t_w/\tau])\right\}, \tag{8}$$

where

t_w = the time of wetness per period.

The deposition can also be calculated from analysis of the dew if the fate of the dissolved gas is known. The deposition per wet period in terms of dew parameters is calculated by the following equation:

$$D_x^{(2)} = \frac{(x)_{dew} V_{dew}}{A_p}, \tag{9}$$

where

$(x)_{dew}$ = the concentration of x in the dew,
V_{dew} = the amount of dew produced during a wet period, and
A_p = the area per test panel.

If the compound under investigation deposits readily onto the wet panel and can be associated with a particular dew ion, then both Equations (8) and (9) can be used to calculate the deposition. Equality of the two depositions establishes a mass balance for the system.

Approximate values for the dry deposition velocities can be obtained by equating the two expressions for the deposition (Equations (8) and (9)) and solving for the deposition velocity. The result is

$$v_d^{(2)} = \frac{(x)_{dew} V_{dew}}{[x_w] A_p t_w}, \tag{10}$$

where it has been assumed that the second term in Equation (8) can be neglected. (Calculations show that this approximation introduces at most a 10% error.) Equation (10) can be used to calculate the dry deposition velocity of compounds that readily adsorb onto a wet surface as well as weakly adsorbing species as long as the fate of the dissolved compound is known.

Analysis of Rain Rinse Data

The concentration of Zn in the rain rinse can be interpreted as a rain flux. The concentration of Zn in nmol/mL is equal to the Zn rain flux in nanomoles/cm^2-cm$_R$, i.e., the number of nanomoles of Zn dissolved into the rain per cm^2 of panel per cm of rain. The amount of Zn corroded by l_R cm of rain is

$$R_{zn} = [Zn_R] l_R, \tag{11}$$

where

$[Zn_R]$ = the concentration of Zn in the rain rinse, and
R_{zn} = the Zn corrosion expressed as a deposition.

RESULTS

NO_2 Exposure Experiment

The experimental conditions and results for the short-term NO_2 exposure experiment are given in Table 1. The average concentration of NO_2 during the dry periods was 649 ppb which decreased to 627 ppb in the presence of dew, thus yielding (according to Equation (7)) a value of 0.05 cm/s for the dry deposition velocity. Both NO_2^- and NO_3^- were detected in the dew with the NO_2^- concentration $\left(300 \frac{\text{nmol}}{\text{ml}}\right)$ representing 95% of the NO_X^- concentration. Trace amounts of $SO_4^=$ were found in the dew. A value of $140 \frac{\text{nmol}}{\text{ml}}$ was found for the Zn dew concentration. Equation (10) yields a value of 0.06 cm/s for the NO_2 dry deposition velocity, in reasonable agreement with the value found from the decrease in gas phase concentrations.

A separate NO_2 exposure experiment was conducted to determine whether the amount of NO_2 deposited on the surface during a dry period could be ignored relative to that adsorbed in the presence of dew. It was found that saturation occurs on a dry galvanized steel surface and that the adsorbed NO_2 saturation surface density was approximately 2 nmol/cm^2. The saturation density is less than 5% of the amount of NO_2 deposited per 7 h of dew $\left(41 \frac{\text{nmol}}{\text{cm}^2}\right)$, and therefore its contribution can be ignored.

Comparison of the NO_2 dry deposition velocity with that found for SO_2 under similar conditions (v_d (SO_2) = 0.8 cm/s; Table 4) indicates a substantial difference in the processes of uptake of the two gases on the test panels. The gas phase resistances for both compounds are expected to be essentially the same. Therefore, the difference between the dry deposition velocities is likely due to a difference in the aqueous reaction and diffusive mechanisms that take place on the metal surface covered by a thin film of moisture. The disparity in velocities is consistent with the recent findings of Lee and Schwartz (18), who evaluated the rate of uptake of NO_2 by surface water. They found that the NO_2 deposition velocity was controlled by aqueous phase mass transport and/or reaction. In addition, Lee and Schwartz found that NO_2 reacts with liquid water according to the following reaction:

$$2\,NO_2\,(g) + H_2O\,(l) \rightarrow 2H^+ + NO_2^- + NO_3^-.$$

This reaction cannot explain the results of the exposure experiment since the dominant NO_X^- compound is NO_2^-. This result may not be surprising since here the reactions took place on a reactive Zn surface.

Judeikis *et al.* recently investigated the uptake of NO_2 on a series of surfaces (19). They found that the identity of the dominant NO_X^- species in the reaction products depended on the chemical

composition of the surfaces. Ten Brink *et al.* found that the presence of Zn particulates greatly enhanced the production rate of nitrous acid (HONO) in air containing NO_2 (20).

The chemical composition of the dew can be clarified by noting that

$$\phi = \frac{[Zn]}{0.5\,[NO_x^-] + [SO_4^=] + S} = 0.75, \qquad (12)$$

where S is the solubility of $ZnCO_3$. If $\phi = 1$, the chemical composition is consistent with a mixture of zinc nitrate ($Zn(NO_3)_2$), zinc nitrite ($Zn(NO_2)_2$), $ZnCO_3$, and $ZnSO_4$. The proposed minor compounds $Zn(NO_3)_2$ and $ZnSO_4$ are water soluble and can be produced by the reactions of the strong acids HNO_3 and H_2SO_4 with either the base metal or the relatively insoluble corrosion products $ZnCO_3$ and $Zn(OH)_2$. The solubility of $ZnCO_3$ is included to take into account the possibility that some of the Zn may have arisen from the dissolution of the corrosion products that is not associated with reactions with acidic components of the dew. This contribution is expected to be present even in the absence of air pollutants other than CO_2.

The presence of rather large amounts of NO_2^- suggests that $Zn(NO_2)_2$ is produced; however, no information on the proposed compound could be found in the literature. If produced, the formation mechanism is likely a reaction of the corrosion products with HONO. The fact that HONO is a weak acid could explain why a value less than 1 is found for ϕ, since the calculation assumes that all of the NO_2^- is associated with Zn. If the production of $Zn(NO_2)_2$ is ignored, a value of 1.5 is found for ϕ. Under these circumstances, there is excess Zn in the dew that cannot be accounted for.

The experimental results suggest that the deposition of NO_2 into dew accelerates the corrosion of galvanized steel; however, it is difficult to establish this definitively because the concentration of dissolved NO_X^- in the dew is small, thus its contribution to the production of soluble Zn corrosion products is similar in magnitude to that associated with the dissolution of the relatively insoluble corrosion products in non-acidic aqueous solutions.

The rain rinse data results are shown in Table 1. The Zn concentration in the rain rinse with a pH of 3.5 was 13 times the value obtained from the analysis of the clean rain (pH of 5.6) rinse.

C_3H_6/NO_x + hv Exposure Experiment

The steady state reactant and product distribution in this experiment contained a complex mixture of oxidants whose concentrations were, in general, much larger than those that occur under ambient conditions but likely contains many of the air pollutants that are present during smog conditions (Table 2).

The steady state NO_X, PAN, and O_3 concentrations were not very stable, and the cited dry concentration values are the average values for the entire experiment, i.e., $[x_d] \approx [x_w]$. The quantity NO_X-PAN was calculated to obtain an estimate of the NO_2 concentrations. It was assumed that the NO_X monitor responded to PAN as NO_X. The HNO_3 concentrations were so small (7 ppb) that it was not possible to observe a decrease in the concentration during periods of wetness. NO_2^-, NO_3^-, $SO_4^=$, HCHO, and Zn were detected in the dew.

Equation (10) is used to calculate the dry deposition velocity for NO_2. It is assumed that all of the NO_2^- in the dew came from the dissolution of NO_2. A value of 0.03 cm/s is found for the deposition velocity. To calculate the dry deposition velocity for HNO_3, it is assumed that the source of dew NO_3^- was the dry deposition of HNO_3. The calculated value, 2.0 cm/s, appears high relative to the velocities of other soluble gases such as HCHO (see Tables 2 and 4) and likely reflects that HNO_3 can be adsorbed onto a dry surface. Evidence to substantiate this point appears in the next section. It is also possible that some of the NO_3^- and/or NO_2^- arose from the deposition of small amounts of PAN; however, the ionic fate of dissolved PAN is not known and therefore more information is required for an assessment of its role in atmospheric corrosion.

The CH_3CHO deposition velocity is found using Equation (7). The value obtained is 0.35 cm/s. Deposition velocities for HCHO are found using Equations (7) and (10). Equation (7) yields a value of 0.93 cm/s whereas the dry deposition velocity based on the dew analysis is 0.35 cm/s. The discrepancy indicates either that there is an error in one of the measurements (gaseous HCHO or aqueous HCHO) or that the dissolved HCHO undergoes reaction. It is not apparent that any measurement errors were made, and, as will be shown, the discrepancy does not occur when analyzing the HCHO data for the $C_3H_6/NO_x/SO_2$ experiment. The difference in velocities can be explained if it is assumed that some of the dissolved HCHO is oxidized to formic acid (HCOOH), a species that is not detected by the chromotropic acid method. An estimate of the amount of HCOOH produced can be obtained by subtracting the amount of HCHO deposited, calculated by the dew analysis method (Equation (9)) from the amount deposited using Equation (8). The results are as follows:

$$D_{HCHO} = 380 \frac{nmol}{cm^2} \text{ (Equation (8)), and}$$

$$D_{HCHO} = 133 \frac{nmol}{cm^2} \text{ (Equation (9)).}$$

The difference in deposited HCHO converted into an equivalent HCOOH concentration gives a value of $1748 \frac{nmol}{ml}$.

The chemical composition of the dew is analyzed in the same way as in the NO_2 experiment. The presence of NO_X^- in the dew suggests, as before, the formation of $Zn(NO_2)_2$, $ZnCO_3$, and $Zn(NO_3)_2$. Assuming that these, plus a small amount of $ZnSO_4$, are the only Zn compounds in the dew, produces the following result for ϕ:

$$\phi = \frac{[Zn]}{0.5\,[NO_x^-] + [SO_4^=] + S} = 3.0.$$

The large value for ϕ indicates the presence of other soluble Zn compounds for which a prime candidate is zinc formate ($Zn(CHOO)_2$), a well known water-soluble compound that is formed when HCOOH reacts with Zn. If the estimated value for the $CHOO^-$ concentrations is included in the expression for ϕ, the following result is obtained:

$$\phi = \frac{[Zn]}{0.5\,[NO_x^-] + 0.5\,[CHOO] + [SO_4^=] + S} = 0.55.$$

The introduction of $Zn(CHOO)_2$ narrows the difference between the calculated value for ϕ and the theoretical value of 1 for which the soluble Zn compounds have been totally accounted. However the introduction of $CHOO^-$ results in more anions than can be accounted for by the Zn concentration. A possible explanation is that HCOOH is a weak acid and that some of the acid remained undissociated. The presence of $CHOO^-$ in the dew is consistent with the findings of Knotkovà, who observed that HCHO accelerated the corrosion of a number of metals, including galvanized steel, and that the corrosion products contained $CHOO^-$ (21). In addition to HCHO oxidation in solution, the possibility exists that CH_3CHO coud be oxidized to acetic acid. However, no measurements were made during the experiments to evaluate this reaction.

Table 3 shows the rain rinse data for the experiment. The Zn dissolved per rain event increased by nearly a factor of 7 as the pH was decreased from 5.6 to 3.5, a result in qualitative agreement with that found in the NO_2 experiment. The Zn corrosion determined by weight loss measurements (D_{Zn}^{WL}) and the total amounts of Zn corrosion induced by dew and rain are also shown in Table 3. The total Zn lost due to dew (D_{Zn}^T) is obtained by multiplying $D_{Zn}^{(2)}$ by 28, the number of dew cycles in the exposure experiment. Total Zn corrosion caused by rain (R_{Zn}^T) is found by multiplying the average Zn rain rinse concentration by the total rainfall (14.2 cm). The Zn corrosion determined by weight loss is consistent with the rain rinse data. The maximum Zn corrosion took place on those panels sprayed with rain having a pH of 3.5. For each exposure condition, the sum of the Zn found in the rain and dew is less than that found by weight loss. The difference is likely due to the presence of an insoluble protective layer that is not dissolved in the dew or rain but is dissolved by the cleaning process.

$C_3H_6/NO_x/SO_2$ + hν Exposure Experiment

Table 4 contains the experimental conditions and results for the irradiated $C_3H_6/NO_x/SO_2$ mixture. The chemical composition was similar to the steady state mixture of the irradiated C_3H_6/NO_x system except for the presence of SO_2 and its oxidation products.

No decreases were found in the NO_x, O_3, or PAN concentrations during dew formation. The NO_2 and HNO_3 deposition velocities were calculated using the same method as was employed in the C_3H_6/NO_x experiment. The NO_2 dry deposition velocity was 0.02 cm/s, and the deposition velocity for HNO_3 was 2.0 cm/s, both in reasonable agreement with the previous results. Analysis of the dry panel, deionized H_2O rinse indicated that as much as 60% of the HNO_3 deposition took place during the dry periods. If this contribution is taken into account, Equation (11) yields a value of 0.7 cm/s for the HNO_3 dry deposition velocity.

The SO_2 dry deposition velocity based on the decrease in gas phase SO_2 concentration was 0.77 cm/s. The value obtained from the dew analysis was 0.82 cm/s. The approximate equality of the deposition velocities demonstrates a reasonable mass balance for the sulfur species. Good agreement is also found for the HCHO dry deposition velocities $\left(0.45 \frac{cm}{s}, 0.47 \frac{cm}{s}\right)$. Analysis of the dry panels showed no evidence for substantial HCHO deposition to dry surfaces.

The dominant SO_x species in the dew was $SO_3^=$. This result differs from that found in single component SO_2 exposure experiments where the dominant species was $SO_4^=$ (12). It appears that a reaction took place which tied up the $SO_3^=$ or its precursor bisulfite (HSO_3^-) and prevented it from oxidizing to $SO_4^=$. The result that the $SO_3^=$ to aqueous HCHO ratio is 1.1 is consistent with the formation of a $HCHOHSO_3^-$ adduct, i.e.,

$$HCHO + HSO_3^- \rightarrow HCHOHSO_3^-,$$

the anion associated with hydroxymethane sulfonic acid. This species is detected as $SO_3^=$ by ion chromatography and as aqueous HCHO by the chromotropic acid method. Munger *et al.* have recently found this species present in the Los Angeles fog samples (22).

The dew molar ratios suggest that the dew consisted of a mixture of $Zn(NO_2)_2$, $Zn(NO_3)_2$, $ZnCO_3$, $ZnSO_4$, and $Zn(HCHOHSO_3)_2$. The corresponding value for ϕ is determined as follows:

$$\phi = \frac{[Zn]}{0.5\,[NO_x^-] + [SO_x^=] + 0.5\,[HCHOHSO_3^-] + S} = 1.0,$$

where it has been assumed that the $HCHOHSO_3^-$ concentration is equal to the aqueous HCHO concentration, and the $SO_x^=$ concentration is equal to the sum of the $SO_4^=$ concentration and the difference between the aqueous HCHO concentration and the $SO_3^=$ concentration. This result shows

that soluble Zn dew compounds can be completely accounted for by the above mentioned mixture. The presence of the $HCHOHSO_3^-$ ion indicates that the contributions of dissolved HCHO and SO_2 to corrosion are not additive. However, it is not clear to what extent the adduct would form under ambient conditions where other reaction pathways may be important.

DISCUSSION

The results of the exposure experiments suggest that compounds other than SO_2 should be considered when designing and analyzing galvanized steel corrosion field data. These compounds include HNO_3, HCHO, and possibly NO_2. It was not possible to determine whether other photochemical oxidants such as CH_3CHO, PAN, H_2O_2, or O_3 accelerate corrosion.

SO_2, NO_2, and HCHO will deposit on a dry surface until saturation occurs. In the case of SO_2, previous work has shown that the saturation surface density is similar to that of a monolayer of adsorbed SO_2 (12). During wet periods, the dry deposition velocities of SO_2 and HCHO will be controlled essentially by the gas phase resistance of the atmosphere. However, the NO_2 deposition velocity is controlled by the surface resistance. The deposition of HNO_3 is more difficult to parameterize because, apparently, it is readily adsorbed on a dry surface. Each of the above mentioned compounds can form acids in dew that react to produce soluble Zn corrosion products. The corrosion induced per mole of compound deposited depends on the stoichiometric coefficient (γ_i) for the reaction. The coefficients for the compounds detected in this study and the experimentally determined average dry deposition velocities for the precursor gas phase species are given in Table 5. It has been assumed that the acids produced in the dew are totally dissociated and react stoichiometrically with the layer compounds. The presence of the $HCHOHSO_3^-$ adduct in the dew produced in the irradiated $C_3H_6/NO_x/SO_2$ mixture indicates the possibility that antagonistic and/or synergistic effects will have to be considered when evaluating field data.

It has been shown that rain can induce Zn corrosion. Analysis of the rain rinse samples showed that the corrosion rate increased as the pH of the incident spray decreased. However, it is difficult to extrapolate the results to atmospheric conditions because the laboratory spray conditions were such that the residence time of a spray droplet was on the order of seconds. It is not clear whether there was adequate time for the reaction to take place.

The Zn corrosion products in the dew represent only the soluble corrosion products. Information on the insoluble corrosion products was obtained only in the C_3H_6/NO_x experiment in which weight loss determinations were made. It was found that the total Zn corrosion determined by the weight loss method was larger than that found in the dew and rinse. The difference is equal to the amount of insoluble corrosion product formed.

The results of the experiments suggest that the amount of soluble Zn corrosion product formed can be estimated if the deposition of the precursor gas phase species can be determined. However, the question of what controls the formation of the protective layer has not been discussed. In the next section, a model for the atmospheric corrosion of galvanized steel is formulated in which

both the role of deposition and the parameters that control both the formation of soluble and insoluble products are addressed. For the remaining discussion, the term 'insoluble corrosion products' will be used to denote the compounds $ZnCO_3$ and $Zn(OH)_2$ that comprise the protective layer.

Formulation of Corrosion Model

The corrosion products formed on galvanized steel consist of insoluble compounds ($Zn(OH)_2$, $ZnCO_3$, etc.) and soluble compounds ($ZnSO_4$, $Zn(NO_3)_2$, etc.). First, the time evolution of the insoluble component will be addressed. The corrosion will be expressed in terms of change in surface thickness due to corrosion product formation.

As discussed previously, under clean air conditions, a protective layer will form on the surface inhibiting further corrosion. The time development of the protective insoluble corrosion product layer can be described by the following differential equation:

$$\frac{dT}{dt} = \frac{\alpha}{T} f, \tag{12}$$

where

T = the thickness of the insoluble corrosion product layer,
f = the fractional time of wetness, and
α = a diffusion coefficient.

The parameter f is introduced to take into account the fact that corrosion only takes place when the surface is wet. The solution to Equation (12) is as follows:

$$T(t) = \sqrt{2 \alpha f t}, \tag{13}$$

where t is the total exposure time. T is a parabolic function of the exposure time controlled by the value of the diffusion coefficient α, whose value is not known, but is likely to be related to the diffusion coefficients that describe molecular transport through the solid protective layer.

The results of the experiments reported here are consistent with a model in which acidic components in the rain and dew react with the insoluble corrosion products. If it is assumed that all deposited compounds react stoichiometrically with the layer compound, Equation (12) can be re-expressed as Equation (14):

$$\frac{dT}{dt} = \frac{\alpha}{T} f - \beta, \tag{14}$$

where

$$\beta = A \left\{ f \sum_{i=1}^{N} \gamma_i v_{di} [x_i] + l(0.5[H^+] + S) \right\}, \tag{15}$$

and

- N = the number of gas phase species that deposits onto the surface and participates in corrosion;
- $[x_i]$ = the gas phase concentration of air pollutant i;
- v_{di} = the dry deposition velocity of air pollutant i;
- γ_i = the stoichiometric coefficient for the reaction between the dissolved air pollutant i and the layer compound;
- l = the amount of rain per unit time;
- $[H^+]$ = the rain concentration of H^+;
- S = solubility of $ZnCO_3$; and
- A = a constant that converts the loss of material in moles per unit area to change in thickness.

The wet deposition component of β has been divided into a "clean" rain contribution and a term that represents the corrosion induced by the acidic components of the rain. The latter component is expressed in terms of H^+ concentration in the rain and assumes that it takes two H^+ ions to corrode one Zn atom. This mechanism is essentially identical to the one proposed for the production of soluble Zn corrosion products by deposition of acidifying air pollutants into the dew. The "clean" rain term contains the contribution due to the solubility of $ZnCO_3$ in H_2O. This type of term has not been included for dry deposition because, at least to a first approximation, the volumes of dew produced under ambient conditions, as opposed to that produced in the present laboratory, would be small. Therefore, the clean dew contribution can be ignored relative to that of the dew acids. More research is required to establish this assumption. In addition, it has been assumed that the two contributions to wet deposition-induced corrosion are additive. This may be an over-simplification of what actually occurs under ambient conditions.

The solution to Equation (14) is as follows:

$$T(t) = T_o\left\{1 - exp\left[-\frac{(T(t)+\beta t)}{T_o}\right]\right\}, \tag{16}$$

where $T_o = \frac{\alpha f}{\beta}$ and is the steady state thickness of the insoluble corrosion product layer. The total corrosion $C(t)$ is obtained by adding the contribution of the soluble corrosion products to $T(t)$, i.e.,

$$C(t) = T_o\left\{1 - exp\left[-\frac{(T(t)+\beta t)}{T_o}\right]\right\} + \beta t. \tag{17}$$

Equation (16) is a transcendental equation that must be solved iteratively. The corrosion at exposure time t is the sum of the soluble and insoluble components; however, the insoluble contribution depends on the amount of soluble products produced via its dependence on βt.

The developed model differs significantly from the linear model represented by Equation (3). Analysis of galvanized steel corrosion field data shows that, in general, the corrosion is not a linear function of exposure time, particularly for short exposure times (5). The development of the steady state protective layer is nonlinear in time, and only after this layer is established will the corrosion appear to increase linearly. The thickness of the protective layer depends on the environmental condition. Under clean air conditions a thick protective layer will form; however, under highly polluted conditions (large β), T_o will be small and the corrosion will be dominated by the soluble contribution to Equation (17).

The proposed model represents a first step in the development of a corrosion model for galvanized steel. To validate the model, detailed testing of model predictions versus results of field exposure studies is required. Such an effort is presently being conducted in our laboratory.

TABLE 1. RESULTS OF NO_2 EXPOSURE EXPERIMENT

Total Exposure Time: 25 h
Total Time of Wetness: 14 h (7-h periods)
Air Temperature: 26°C
Plate Temperature When Wet: 10°C
Rain Frequency: Once at the end of the experiment
Amount of Rain per Event: 0.59 cm

Gas Phase

x	$[x_d]$ (ppb)	$[x_w]$ (ppb)	$v_d^{(1)}\left(\frac{cm}{s}\right)$	$v_d^{(2)}\left(\frac{cm}{s}\right)$
NO_2	649	627	0.05	0.06

Dew

x	$[x]\left(\frac{nmol}{ml}\right)$	$D_x^{(2)}\left(\frac{n\,mol}{cm^2}\right)$
NO_2^-	203	39
NO_3^-	11	2
NO_X^-	214	41
$SO_4^=$	12	2
Zn	149	29

Rain

pH	$[Zn]\left(\frac{nmol}{ml}\right)$	$R_{Zn}\left(\frac{n\,mol}{cm^2}\right)$
5.6	2	1.2
3.5	26	15

TABLE 2. RESULTS OF C_3H_6/NO_X + hν EXPOSURE EXPERIMENT

Total Exposure Time: 336 h
Total Time of Wetness: 196 h (7-h periods)
Air Temperature: 32°C
Plate Temperature When Wet: 10°C
Rain Frequency: After four and nine days exposure and at the end of the experiment
Amount of Rain per Event: 4.7 cm

Gas Phase

x	$[x_d]$ (ppb)	$[x_w]$ (ppb)	$v_d^{(1)}\left(\frac{cm}{s}\right)$	$v_d^{(2)}\left(\frac{cm}{s}\right)$
O_3	134			
PAN	57			
NO_X-PAN	359			0.03
HNO_3	7			2.0
HCHO	621	389	0.93	0.33
CH_3CHO	254	207	0.35	

Dew

x	$[x]\left(\frac{nmol}{ml}\right)$	$D_x^{(2)}\left(\frac{n\,mol}{cm^2}\right)$
NO_2^-	95	11
NO_3^-	118	15
NO_X^-	213	26
$SO_4^=$	6	1
HCHO	940	133
Zn	590	77

Rain

pH	$[Zn_R]\left(\frac{nmol}{ml}\right)$	$R_{Zn}\left(\frac{n\,mol}{cm^2}\right)$
5.6	4	17
3.5	27	127

TABLE 3. COMPARISON OF Zn CORROSION BASED ON WEIGHT LOSS DETERMINATIONS AND THAT OBTAINED BY ANALYSIS OF DEW AND RAIN RINSE SAMPLES

	$\left(\frac{n\ mol}{cm^2}\right)$		
Exposure Condition	D_{Zn}^{WL}	D_{Zn}^{T}	R_{Zn}^{T}
pH = 5.6 Rain + Dew	2,460	2,160	50
pH = 3.5 Rain + Dew	3,450	2,160	380
Dew Only	2,880	2,160	0

TABLE 4. RESULTS OF $C_3H_6/NO_X/SO_2$ + hv EXPOSURE EXPERIMENT

Total Exposure Time: 25 h
Total Time of Wetness: 14 h (7-h periods)
Air Temperature: 32°C
Plate Temperature When Wet: 10°C
Rain Frequency: No rain events

Gas Phase

x	$[x_d]$ (ppb)	$[x_w]$ (ppb)	$v_d^{(1)}\left(\frac{cm}{s}\right)$	$v_d^{(2)}\left(\frac{cm}{s}\right)$
SO_2	1,190	798	0.77	0.82
O_3	240			
PAN	114			
NO_X-PAN	159			0.02
HNO_3	9			2.0
HCHO	1,550	1,195	0.47	0.45
CH_3CHO	792	715	0.17	

Dew

x	$[x]\left(\frac{nmol}{ml}\right)$	$D_x^{(2)}\left(\frac{n\,mol}{cm^2}\right)$
NO_2^-	35	4
NO_3^-	182	19
NO_X^-	217	23
$SO_3^=$	5,650	595
$SO_4^=$	826	91
$SO_X^=$	6,476	686
HCHO	5,100	560
Zn	4,174	441

TABLE 5. PROPERTIES OF POTENTIAL CORROSION STIMULATORS

Gas Phase	Anion	$v_d\left(\frac{cm}{s}\right)$	γ_i
SO_2	SO_3^*,SO_4^*	0.8	1.0
NO_2	NO_2^-	0.03	0.5
HNO_3	NO_3^-	2.0 (0.7)*	0.5
HCHO	$CHOO^-$	0.6	0.5
$HCHO + SO_2$	$HCHOHSO_3^-$	–	0.5

* The value in parentheses is based on the deposition obtained after subtracting the HNO_3 saturation surface density from the deposition obtained by dew analysis.

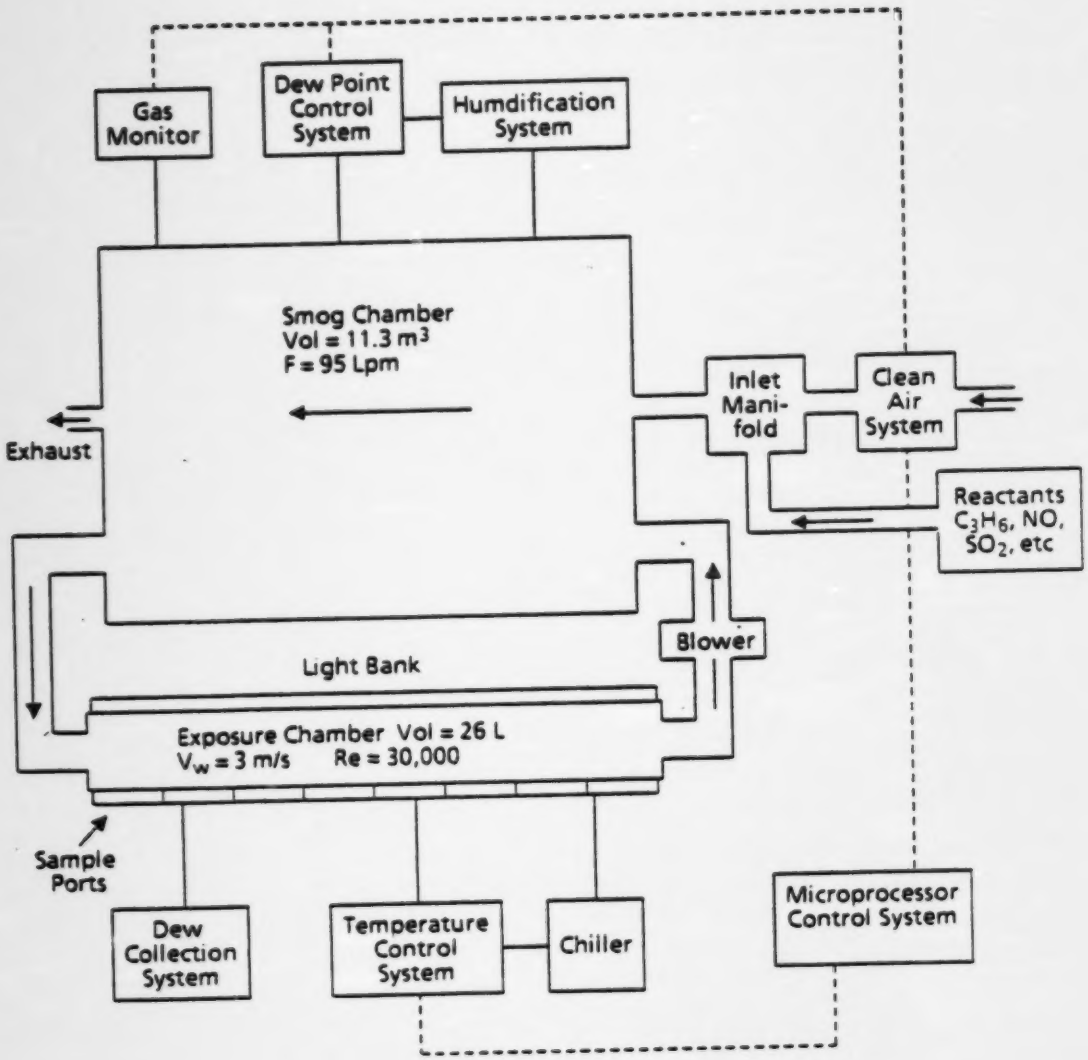

Figure 1. Schematic of Exposure System.

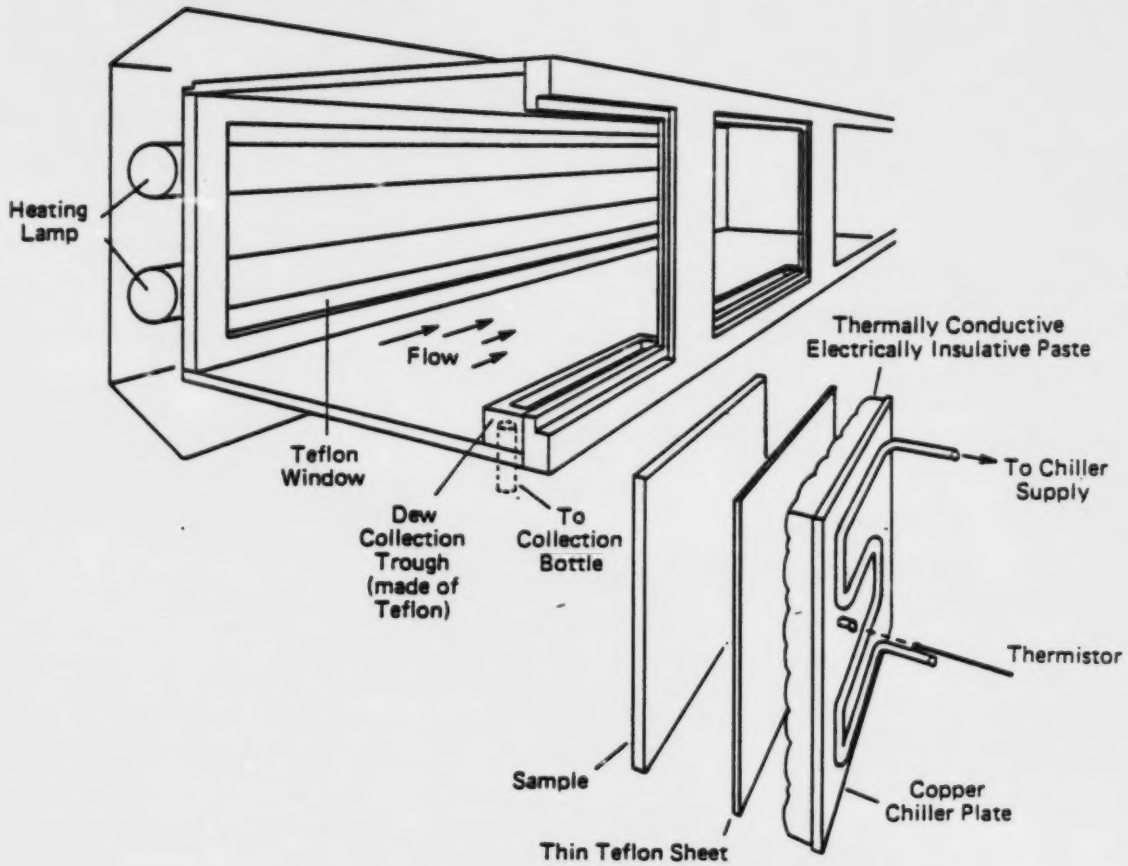

Figure 2. Cross-sectional View of Exposure Chamber.

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